[redacted]




JET PROPULSION LABORATORY

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA

REPORT NO. P65-57

RE-ORDER NO. 65 461

JPL Contract 951003
NASA Contract NAS 7-100

# STUDY OF THE EFFECTS OF ETHYLENE OXIDE-FREON 12 UPON PROPERTIES OF POLYMERS AND METALLIC SURFACES

Interim Status Report Covering 1 October 1964 through 30 April 1965

AEROSPACE GROUP

**HUGHES**

HUGHES AIRCRAFT COMPANY
CULVER CITY, CALIFORNIA

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

# STUDY OF THE EFFECTS OF ETHYLENE OXIDE-FREON 12 UPON PROPERTIES OF POLYMERS AND METALLIC SURFACES

JPL Contract 951003
NASA Contract NAS 7-100

Interim Status Report Covering
1 October 1964 through 30 April 1965

R.F. Rydelek
A.L. Landis

JPL Cognizant Engineer: Herman Harvey

Approved: W.H. Colner
W.H. Colner, Manager
Materials Technology Department

Submitted to: Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, California

Copy Number ________

MATERIALS TECHNOLOGY DEPARTMENT
RESEARCH AND DEVELOPMENT DIVISION
AEROSPACE GROUP
Hughes Aircraft Company · Culver City, California

## FOREWORD

This report summarizes work performed under Jet Propulsion Laboratory Contract 951003, NAS 7-100, "Study of Effects of Ethylene Oxide—Freon 12 upon Properties of Polymers and Metallic Surfaces", during the period October 1, 1964 through April 30, 1965. Mr. Herman Harvey is JPL Cognizant Engineer on this program.

The Hughes Project Engineer is R.F. Rydelek who is also responsible for the Materials Screening portion of the program. The Mechanisms Studies are being conducted by Dr. A.L. Landis.

## ABSTRACT

30561

The compatibility of approximately 75 commercial polymeric products with gaseous and dry heat sterilization regimes is to be determined in this program. The effect of subjecting materials to a dry heat cycle (108 hours, 145°C) both before and after exposure to a 12% ethylene oxide—88% Freon 12 mixture for 24 hours at room temperature (74°F) and 24 hours at 104°F were evaluated by measuring changes in physical, mechanical, and electrical properties. A concurrent mechanism study was conducted on representative polymer systems to provide insight into the nature of the gas-material interaction.

Work accomplished during the first six months of this program indicates that silicone and epoxy polymers, both pure and commerical grade, are capable of physically adsorbing one to four percent by weight of sterilant gas. Silicone compounds release all but a fraction of a percent of sorbed gas when exposed to vacuum, with little change in physical or mechanical properties. Epoxy compounds retain a lesser amount of gas in the sorbed state but show a more pronounced change in properties suggesting that a chemical reaction also occurs during exposure. In most cases, the amount of residual sterilant remaining in the sorbed state after exposure to gas and vacuum decreased when materials were processed through a subsequent heat step.

The exposure of silicone materials to sterilant gas and then to extended heat cycling produced a greater loss of tensile properties than exposure to heat followed by gas. This effect suggests that chemical interaction is favored by the gas-heat regime.

Of the materials tested to date, none has displayed sufficient degradation to classify it as incompatible with the sterilization regimes used in this program.

Author

## CONTENTS

ILLUSTRATIONS

## TABLES

# I. PROGRAM PLAN

## INTRODUCTION

The advent of planetary probes and landing vehicles has focused attention on the need for biological sterilization of spacecraft. One of the major mission objectives of planetary exploration, the detection of extraterrestrial life forms, may not be realized if viable earth-type-organisms are carried aloft on non-sterile craft. Total mission failure may result, however, if the performance of spacecraft systems or components is degraded by the decontamination process.

Dry heat cycling and gaseous chemical sterilants are highly effective in achieving biological sterility but are also capable of producing marked changes in material properties. The compatibility of system materials with sterilization procedures must be established to gain the optimum confidence in performance reliability of spacecraft systems. Only materials whose properties are not seriously affected by contact with the 12% ethylene oxide—Freon 12 sterilant gas mixture can be used for sterilizable spacecraft. This gas mixture is highly penetrative and can cause chemical and physical changes not only on the surface of materials, but throughout their entire mass.

The primary objective of this program is to provide quantitative information on the compatibility of polymeric products and a select group of metallic materials with a 12% ethylene oxide—88% Freon 12 gas mixture. Exposure to gas alone is not sufficient to insure sterility. Effective in-depth sterilization of spacecraft will require exposure of components and systems to heat also; therefore, the compatibility of materials with sterilant gas alone has no practical meaning. All materials screened in this program are subjected to a dry heat cycle before or after ethylene oxide—Freon 12 exposure to approximate conditions encountered by flight hardware during decontamination procedures.

The nature of the gas—material interaction is also under study. In the mechanism portion of the program, representative chemical classes of materials are subjected to sterilant gas,and material behavior analyzed with the aid of infrared, chromatographic, and gas-sorption techniques.

To gain the maximum amount of useful information from the program, the screening and mechanism portions are conducted as parallel efforts. The same polymer classes are studied concurrently so that information from both phases can be used to establish a clearer picture of material behavior, and guide the direction of subsequent testing. Information from the analytical phase can provide insight into the mechanism of material degradation to aid in the development of sterilizable materials.

## LITERATURE SURVEY

To save testing time in the screening portion of the program, a search of the literature was made to establish the compatibility of as many materials as possible with the ethylene oxide-Freon 12 gas mixture.[1] Since a complete literature search of this field was made by Hughes in 1961-1962,[2] it was not necessary to examine the literature prior to 1962. Materials of primary interest in this survey were those appearing on the first list submitted by JPL for test.

A separate survey[3] was made in conjunction with the mechanism study to obtain information on the reactions of ethylene oxide and Freon 12, including sorption characteristics, corrosive effects and susceptiblity to polymerization when in contact with polymeric and metallic materials.

---

[1] R.F. Rydelek, "Literature Review of the Compatibility of Commercial Materials with Ethylene Oxide-Freon 12 Sterilant Gas Mixture," HAC Ref. No. 2748.40/910, JPL Contract 951003, January 1965

[2] M. Willard, V.K. Entrekin, "A Literature Review of the Physical, Chemical, and Biological Properties of Ethylene Oxide—Freon 12 and Its Compatibility with Materials and Components," Surveyor Sterilization Part II, HAC RS-283, March 1962

[3] A.L. Landis, "Literature Review of Mechanisms of Interaction of Ethylene Oxide and Organic and Inorganic Materials," HAC Ref. No. 2748.40/878, JPL Contract 951003, November 1964

Analytical methods for detecting small amounts of ethylene oxide, Freon 12, and water adsorbed in polymers and deposited on metallic surfaces were also investigated. The recent literature provided little compatibility data. The major portion of useable information appeared in material published prior to 1962 and in the reports generated in the experimental study performed as part of the Surveyor Sterilization Program.[4, 5] Applicable information found in the literature survey is summarized below. (References 1 and 3 should be consulted for more detailed information.)

Ethylene oxide is a highly reactive agent capable of participating in a wide variety of reactions and of modifying the physical and chemical properties of many compounds. It is capable of producing marked changes in material properties by reacting directly with base material or with impurities included during the manufacturing process. Two types of reactions are of particular interest in this program; condensation and polymerization. The condensation of ethylene oxide with another compound proceeds by attachment of the broken epoxy ring to an active hydrogen.

Polymerization, catalyzed by bases and other inorganic salts, forms compounds of low volatility, potentially hazardous to electrical contact and thermal control surfaces. Ethylene oxide in the vapor phase is highly penetrative, therefore the permeability of materials is an important factor. Freon 12 has solvent properties and tends to produce swelling in some elastomers. The presence of two fluorine atoms on the Freon molecule, contribute to its high stability and preclude direct chemical reaction with materials under test conditions used in this program.

---

[4]M. Willard, "Compatibility of Materials and Components with Heat and Ethylene Oxide—Freon 12," Surveyor Sterilization Part I, HAC RS-277, January 1962

[5]M. Willard, Further Compatibility Studies of Materials and Components with Ethylene Oxide —Freon 12 and Heat," Surveyor Sterilization Part III, HAC RS-292, July 1962

## MATERIALS PROCUREMENT

Approximately 75 commercial polymeric products are to be screened in this program. Those appearing on the first list submitted by JPL for test are given in Table I. In general, these compounds were ordered directly from the manufacturer to insure "freshness"; formulations which are known to have long term stability such as the epoxy laminates were drawn from in-house stock.

Polymeric materials arriving in the fluid and uncured state were fabricated into sheet form to facilitate testing. Detailed information on formulation techniques are given in the monthly technical progress reports.

Materials such as RTV 108, 140, and 891 are intended for adhesives application and hardening is accomplished by exposure to atmospheric moisture rather than by catalyst. The viscosity of the materials and cure condition requirements make formulation of sheets of even texture and uniform thickness difficult. Alternate test specimen configurations are currently being reviewed.

## PURE POLYMER FORMULATION

The materials studied in the mechanism portion of the program were formulated from pure polymers synthesized in-house or purchased from outside sources. Compounds of known composition were used in curing the polymers.

In the phase of work reported here, emphasis was placed on silicone and epoxy compounds for several reasons:

1. An appreciable number of commercial products are based on these polymers and they are widely used in spacecraft components.
2. The majority of materials appearing on the first JPL list of materials for screening are silicone and epoxy formulations.

A general description of the approach taken in the synthesis of pure polymers is presented below. Detailed information on siloxane synthesis is given in the Appendix of this report. The structure of silicone polymers is a direct function of the mode of synthesis and the experimental procedures are presented in order to define the compounds.

| Product | Manufacturer | Material Type |
|---|---|---|
| AMS 3303/60 | Hadbar | Silicone |
| Epon 828/Z | Shell | Epoxy |
| H-Film | DuPont | Polyimide |
| Laminate MIL-P-13949 | Westinghouse | Epoxy |
| LS-53/70 | Plastic and Rubber Products | Fluorosilicone |
| Micarta H-2497 | Westinghouse | Epoxy-Glass Fiber |
| PR-1930-1/2 | Products Research | Silicone |
| PYRE-MLRK-692 | DuPont | Polyimide |
| RTV 11 | General Electric | Silicone |
| RTV 60 | General Electric | Silicone |
| RTV 108 | General Electric | Silicone |
| RTV 140 | Dow Corning | Silicone |
| RTV 615 | General Electric | Silicone |
| RTV 881 | Dow Corning | Silicone |
| RTV 891 | Dow Corning | Silicone |
| Silastic 1410 | Dow Corning | Silicone |
| Silastic PR 1930-2 | Products Research | Silicone |
| Silgard 182 | Dow Corning | Silicone |
| Stycast 1095/11 | Emerson Cuming | Epoxy |
| Stycast 2651/11 | Emerson Cuming | Epoxy |
| Tedlar 200, Type 30B White | DuPont | Polyvinyl Fluoride |
| Viton B60 and 95 | DuPont | Fluorocarbon |
| 2-218-S417-7 | Parker Seal | Silicone |
| 4000-80 | Hadbar | Silicone |
| 7000-80 | Hadbar | Silicone |

Table I. First JPL list of materials for screening.

Polydimethylsiloxanes are representative of silicone compounds generally used in the formulation of commercial products. The pure polymer (C 1090-60A) was prepared by cohydrolysis of difunctional dimethyl silanes. A similar polymer (C 1090-61A) was prepared by equilibration of cyclic dimethylsiloxanes with sulfuric acid.

Polydimethylphenyl methyl siloxane is also widely used in commercial formulations. The phenyl groups attached to the chain silicone atom impart greater thermal stability to the compound. The pure polymer (C 1962-34) was prepared by cohydrolysis of dimethyldichlorosilane and phenylmethyldichlorosilane.

All of the above polymers were cured with triethoxy methyl silane using a dibutyltin dilaurate catalyst. Epon 828, produced by the Shell Chemical Corporation was selected as a representative epoxy resin. A liquid curing agent, methylnadic anhydride was employed in the formulation of test materials.

The compositions of formulations used in this program are given below. Detailed information on formulation techniques and cure cycles is given in the Appendix.

Silicone Formulation 1

| | |
|---|---|
| polydimethyl phenylmethylsiloxane (C 1962-34) | 100 parts |
| triethoxymethylsilane | 8 parts |
| dibutyltin dilaurate | 2 parts |

Silicone Formulation 2

| | |
|---|---|
| polydimethylsiloxane (C 1090-61A) | 100 parts |
| triethoxymethylsilane | 8 parts |
| dibutyltin dilaurate | 3 parts |

Silicone Formulation 3

| | |
|---|---|
| polydimethylsiloxane (C 1090-60A) | 100 parts |
| triethoxymethylsilane | 8 parts |
| dibutyltin dilaurate | 2 parts |

Silicone Formulation 4

| | |
|---|---|
| polydimethylsiloxane (C 1090-60A) | 100 parts |
| triethoxymethylsilane | 8 parts |

Silicone Formulation 4 (continued)

| | |
|---|---|
| dibutyltin dilaurate | 2 parts |
| powdered silica, 270 mesh | 50 parts |

Epoxy Formulation 1

| | |
|---|---|
| Epon 828 resin | 100 parts |
| methylnadic anhydride | 75 parts |

# II. TESTING

## TEST APPROACH

Materials were screened by exposing them to two separate regimes. Figure 1 lists the individual steps involved in each regime. The dry heat cycle corresponds to that specified in JPL Specification XS0-30275-757A with the exception that individual cycles of up to 40 hours duration were used (with JPL approval). The room temperature and elevated temperature ethylene oxide—Freon 12 exposures are those defined in JPL Specification GMO-50198-ETS.

In the heat-followed-by-gas exposure, material properties were measured after the heat cycle and after each phase of the ethylene oxide exposure. Weight change, volume change and other non-destructive tests were performed on coupons of material which are processed through all steps of the exposure. Two different sets of specimens were used for testing each material, one for heat-followed-by gas, the other for gas-followed-by heat exposures. Three coupons of a material comprised a set for non-destructive tests.

Triplicate sets of coupons for destructive testing of a material were prepared for each exposure regime. In the heat-followed-by-gas regime one set was tested after dry heat cycling, another after room temperature gas exposure (74$^{o}$F) and the third after gas exposure at 104$^{o}$F. In the gas-followed-by-heat regime, materials were tested before gas exposure, after gas exposure, and after dry heat cycling. Specific physical, mechanical, and electrical test methods used for individual materials are listed in Table II.

In the mechanism portion of the program, polymer samples were exposed to pure ethylene oxide vapor in a specially designed sorption apparatus. Sorption and desorption rates were monitored during exposure to gas and subsequent exposure to vacuum. The amount of sterilant retained by test materials after subjection to gas and vacuum served to indicate whether the predominant mechanism involved in the gas-material interaction was a physical adsorption (reversible) or a chemical absorption (irreversible by vacuum exposure).

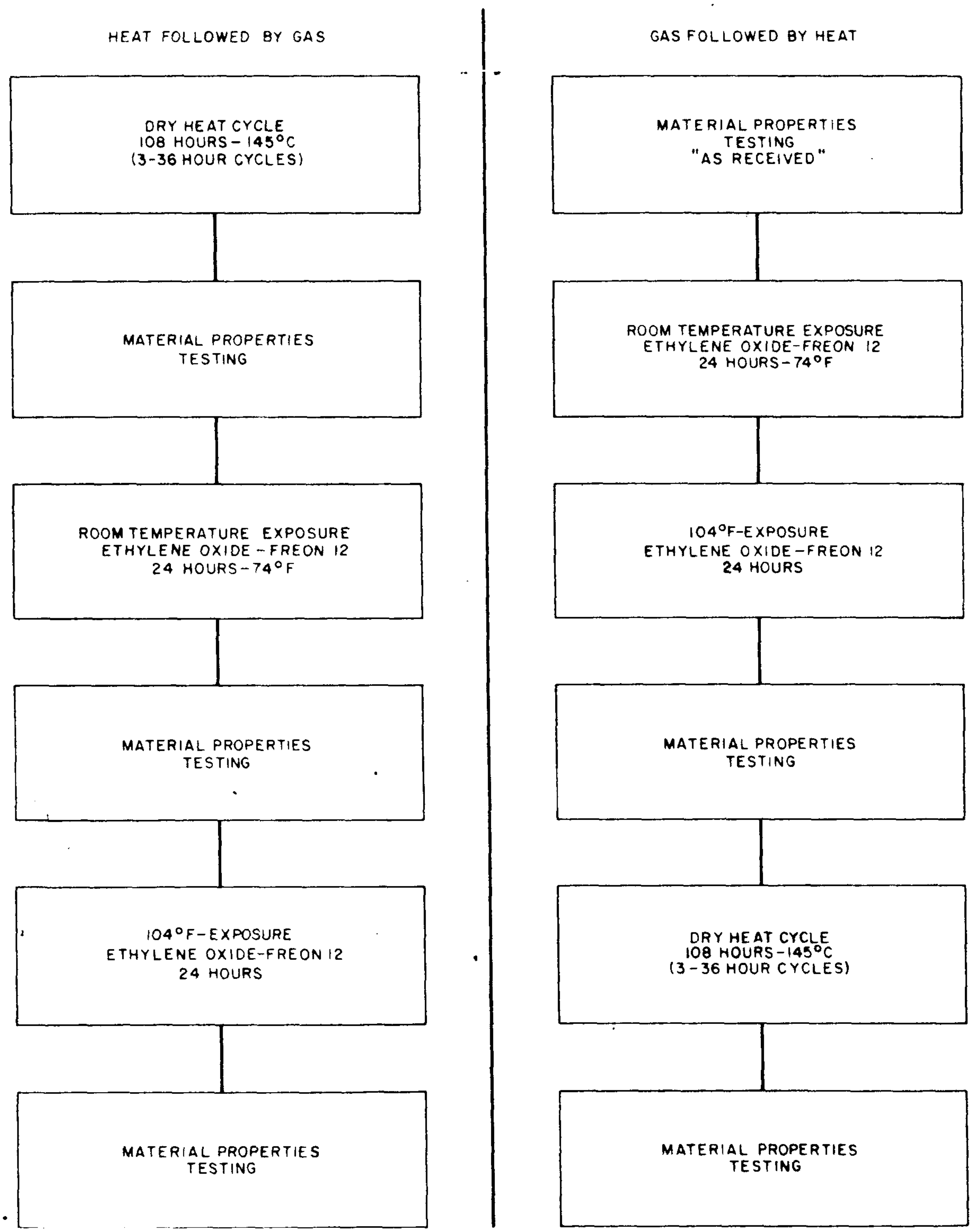



Figure 1. Materials screening regimes.

| Product | Test Method |
|---|---|
| AMS 3303 60 | 1, 2, 5 |
| Epon 828 /Z | 1, 6, 8, 9 |
| H-Film | 1, 3, 7 |
| Laminate MIL-P-13949 | 1, 4, 6, 9 |
| LS-53/70 | 1, 2, 5 |
| Micarta H-2497 | 1, 4, 6, 9 |
| PR-1930-1/2 | 1, 9 |
| PYRE-MLRK-692 | 1, 10 |
| RTV 11 | 1, 9 |
| RTV 60 | 1, 2, 5 |
| RTV 108 | 1, 2, 5 |
| RTV 140 | 1, 2, 5 |
| RTV 615 | 1, 9 |
| RTV 881 | 1, 2, 5 |
| RTV 891 | 1, 2, 5 |
| Silastic 1410 | 1, 9 |
| Silastic PR 1930-2 | 1, 9 |
| Silgard 182 | 1, 9 |
| Stycast 1095/11 | 1, 4, 6, 9 |
| Stycast 2651/11 | 1, 9 |
| Tedlar 200, Type 30B White | 1, 3, 7 |
| Viton B 60 and 95 | 1, 2, 5 |
| 2-218-S417-7 | 1, 2, 5 |
| 4000-80 | 1, 2, 5 |
| 7000-80 | 1, 2, 5 |

| Test Method | ASTM Desig. | Test Description |
|---|---|---|
| 1 | D 257 | Volume and Surface Resistivity |
| 2 | D 412 | Tensile Testing of Vulcanized Rubber |
| 3 | D 624 | Tear Resistance of Vulcanized Rubber |
| 4 | D 638 | Tensile Properties of Plastics |
| 5 | D 676 | Indentation of Rubber Durometer |
| 6 | D 790 | Flexural Properties of Plastics |
| 7 | D 882 | Tensile Properties of Thin Plastic Sheet |
| 8 | D1002 | Strength Properties in Shear by Tension |
| 9 | D1706 | Indentation Hardness of Rigid Plastics |
| 10 | D2197 | Adhesion of Coatings, Paint |

Note: In addition to standard tests given above, weight and volume changes will be measured on all materials, where feasible.

Table II. Physical, mechanical, electrical screening tests.

Infrared spectroscopy was used to study basic changes in polymer structure caused by gas exposure. Transmittance techniques are capable of registering subtle chemical change and are used in preference to less sensitive attenuated total reflectance methods. Thin films of polymeric material were found to be most suitable for the infrared work.

The initial portion of the mechanism study, described in this report, was conducted with pure ethylene oxide. Freon 12 is chemically inert under the test conditions used in this program and its presence introduces another variable. The 12% ethylene oxide—88% Freon 12 mixture will be used for the remaining portion of the program, however.

## TEST EQUIPMENT

The vacuum oven shown in Figure 2 was used to accomplish dry heat cycling. The oven is capable of maintaining a vacuum of 29.5 inches of mercury for extended period. The oven configuration made the use of thermocouples difficult, therefore test temperatures were established as follows: A thermometer was placed at the center of the oven and temperature observed as the oven temperature control settings were increased; when the temperature stabilized at 145$^{\circ}$C, the oven was loaded with materials to simulate a dry heat cycle. A thermometer was placed between sheets of test material at the center of the oven, and the time required to reach 145$^{\circ}$C noted.

Figure 3 is a schematic diagram of the ethylene oxide —Freon 12 exposure apparatus shown in Figure 4. The exposure chamber (1/2 inch steel walls) was wrapped with heating tapes and insulated to provide temperature control for the sterilant gas exposure at 104$^{\circ}$F. Temperature was measured with a shielded thermocouple extending into the chamber.

The apparatus shown in Figures 5 and 6 was fabricated to measure the rate of ethylene oxide sorption by pure polymers and permit degassing of test samples. The all glass apparatus consisted of a manifold, valve system, sample container, manometers, and cold trap. A mercury diffusion pump was used to attain pressures in the range $10^{-4}$ to $10^{-5}$ mm Hg.

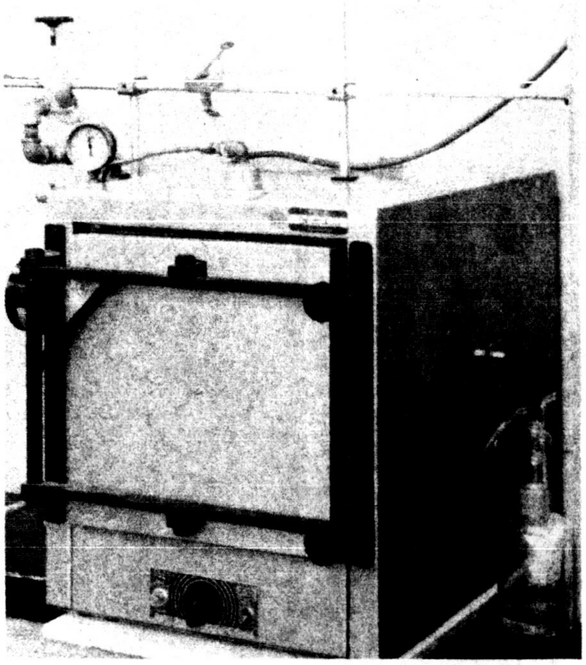


Figure 2. Vacuum oven used for dry heat cycling.

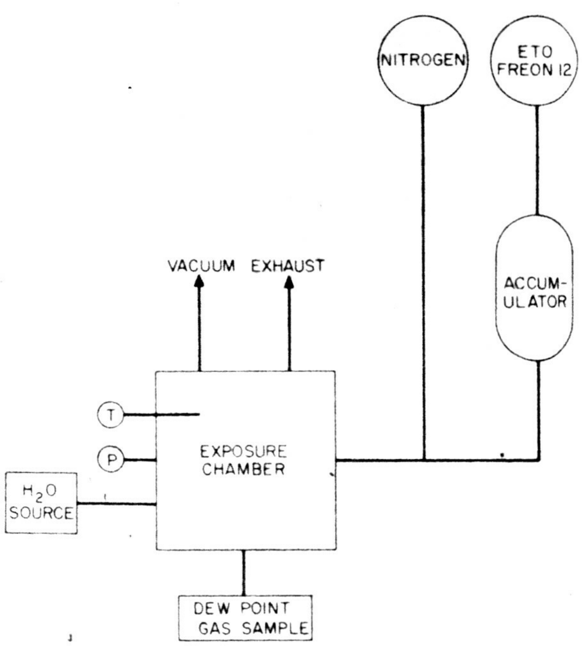



Figure 3. Ethylene oxide-Freon 12 exposure apparatus schematic.

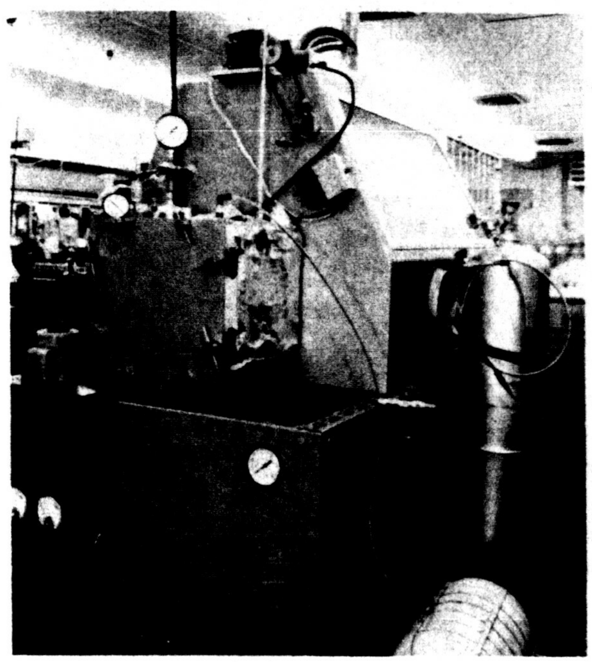


Figure 4. ETO-Freon 12 exposure apparatus.

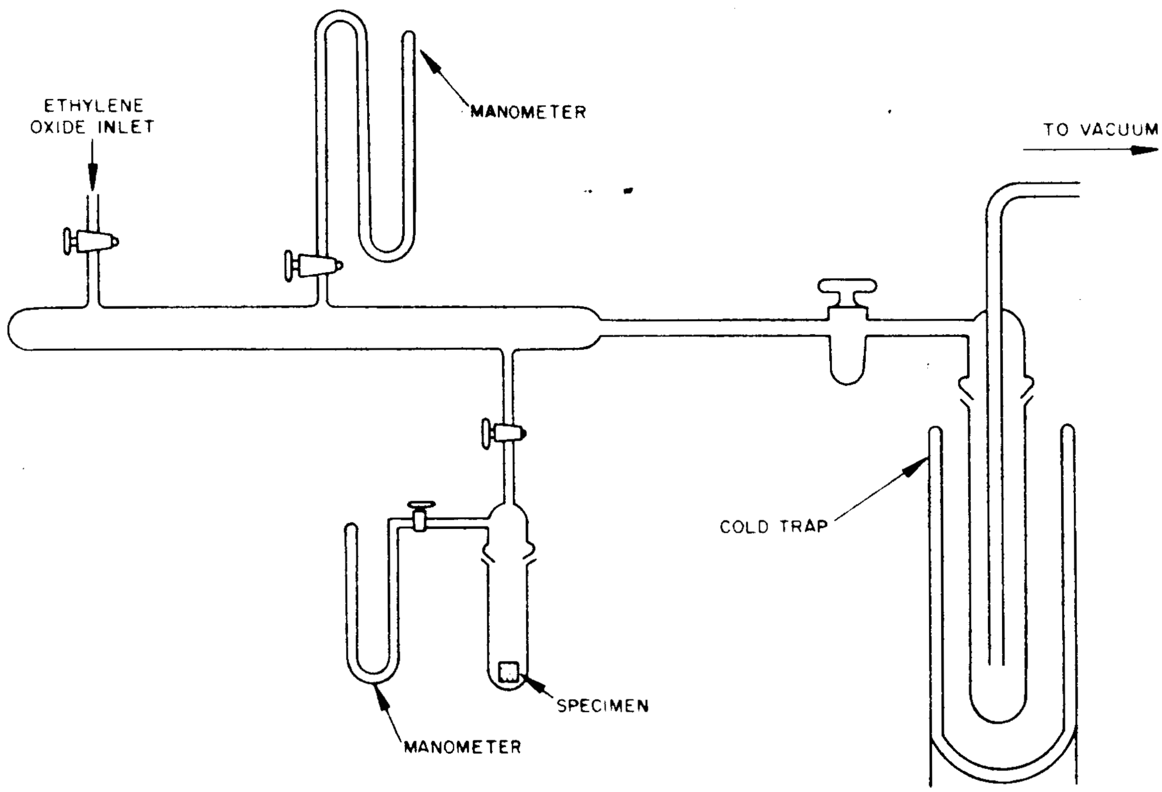



Figure 5. Ethylene oxide sorption apparatus diagram.

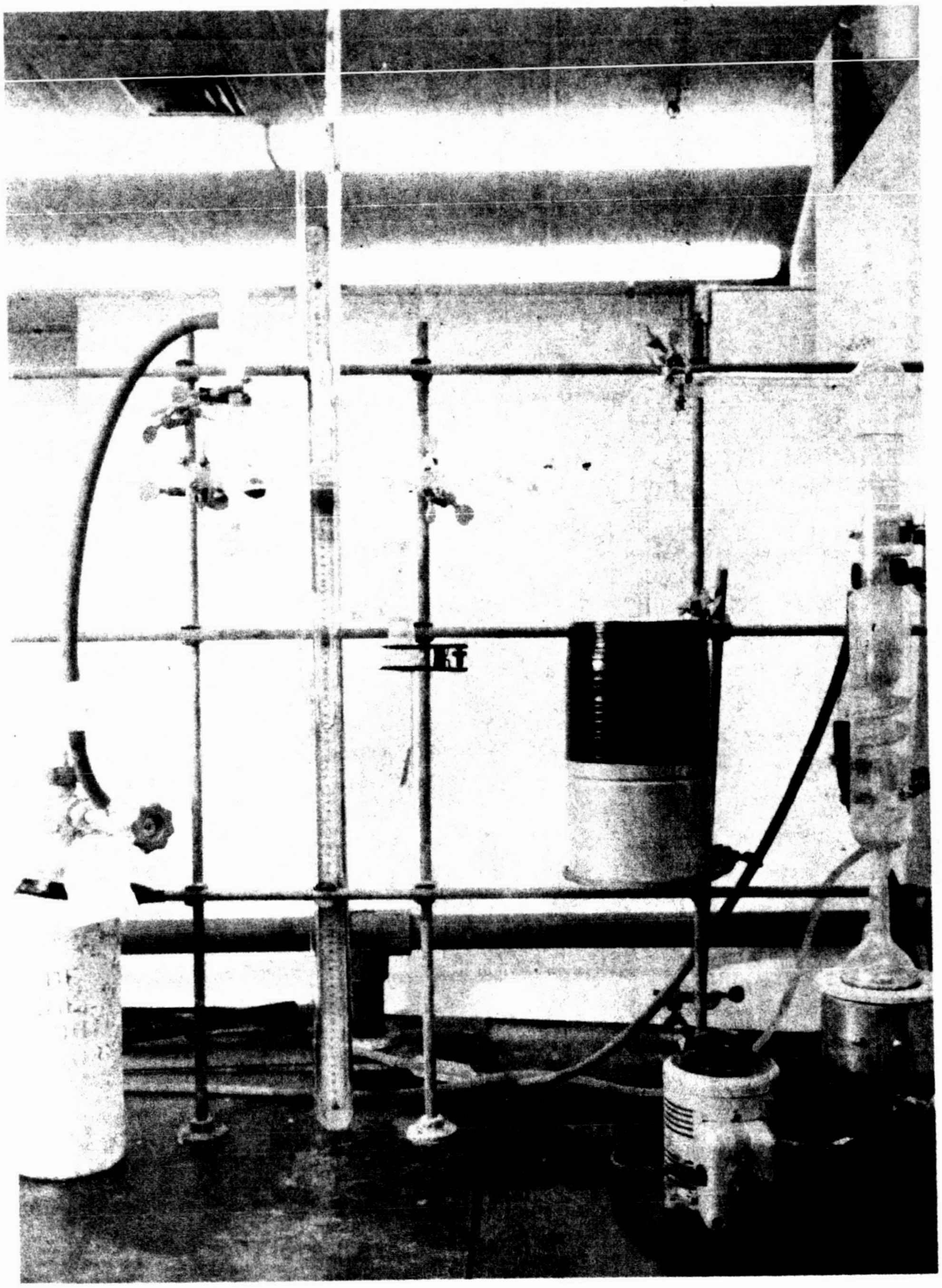


Figure 6. Ethylene oxide sorption apparatus.

A Beckman GC-2 gas chromatograph was used for analysis of system gases. A helium carrier gas pressure of 20 psi and thermal conductivity detector filament current of 200 ma were sufficient to give good resolution with a 12 foot dioctyl isosebacate column modified with 12% Ucon 50 HB-2000. Ethylene oxide elution time is 4 minutes, and Freon 12 is 1.3 minutes with the column at 50°C. A Beckman IR-5 infrared spectrophotometer was used to obtain spectra of pure polymers before and after exposure to ethylene oxide.

## TEST PROCEDURES

### Dry Heat Cycling

Test specimens were placed on metal oven shelves with sufficient spacing to allow free flow of nitrogen around them. The chamber was evacuated, filled with dry, high purity nitrogen, and then evacuated again. After bringing the oven to atmospheric pressure with nitrogen, a low gas flow was established and maintained during the remainder of the test.

At the end of 36 to 40 hours at test temperature, materials were removed from the oven, allowed to stabilize at room temperature, and visually examined. The above procedures were repeated three times, subjecting the test specimens to temperature for a minimum of 108 hours.

### Ethylene Oxide—Freon 12 Gas Exposure (see Figure 4)

Sheets of elastomers and other non-rigid materials were suspended from the top of the exposure chamber, with a minimum of space of 1 inch between them to allow circulation of gas. Small, rigid coupons were arranged around the rim of glass petri dishes and placed on the bottom of the chamber (see Figure 7).

The exposure chamber was evacuated and maintained at 29.5 in Hg for 20 minutes. Ethylene oxide—Freon 12 mixture was slowly bled from the storage cylinder into the evacuated accumulator where it was allowed to temperature stabilize at 10 psig. The evacuated chamber was then opened to a heated water source, until water vapor pressure in the system reached 20 mm Hg. Gas was bled from the accumulator into the exposure chamber until atmospheric pressure was obtained.

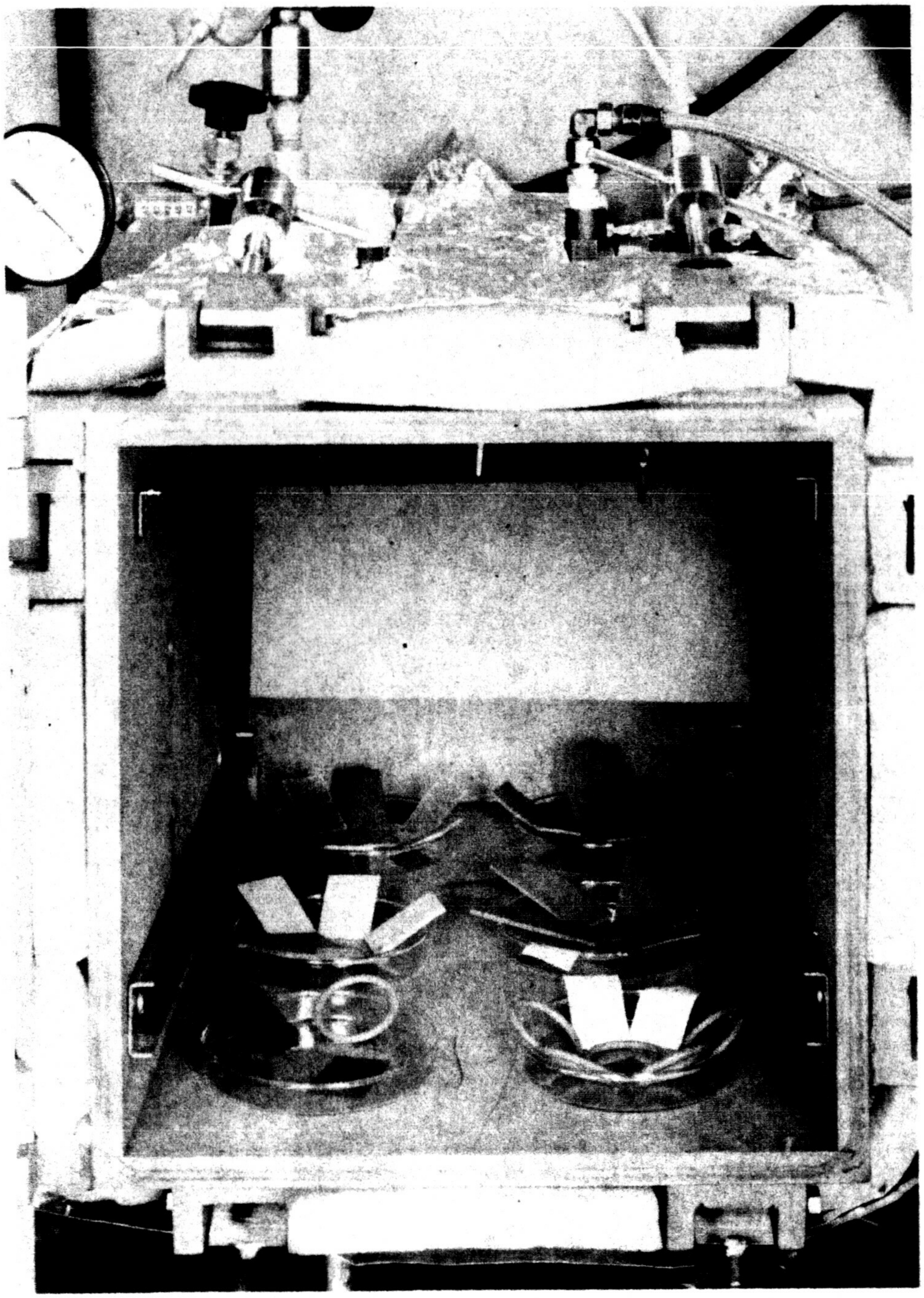


Figure 7. Exposure chamber and samples.

## Dew Point Measurement

The dew point device was evacuated and then opened to the exposure chamber through a valve assembly. The humidity of the gas trapped in the device was determined by adding small pieces of ice to the water in the thermometer well, and stirring vigorously. The temperature at which a haze, denoting water condensation, was observed was taken as the dew point. Dew points in the range $40^{o}F$ to $55^{o}F$ indicate proper chamber humidity for room temperature ($74^{o}F$) gas exposure and $66^{o}F$ to $78^{o}F$ for exposure at $104^{o}F$.

Analysis of gas in the exposure chamber was performed with the gas chromatograph. At the end of the twenty-four hour exposure period, the chamber was flushed with dry nitrogen, evacuated to 29.8 in Hg for 30 minutes and brought to atmospheric pressure with air.

The procedure for exposure at $104^{o}F$ is identical to that described above. The chamber is heated for a period of three hours prior to insertion of test specimens which were allowed to stabilize at chamber temperature for one hour before gas is admitted.

## Sorption Studies

Specimens of test material were placed in the apparatus and degassed by exposure to vacuum. The apparatus was then back filled with ethylene oxide, and the sorption rate obtained by observing the mercury level in the manometer. The ethylene oxide pressure in the test chamber was maintained close to atmospheric by admitting gas as needed. Test specimens were periodically removed from the apparatus and weighed until no increase in weight was detected. Unreacted ethylene oxide was removed from the test material by the application of vacuum. Data from the sorption studies of silicone and epoxy materials are presented in Table X.

## Infrared Studies

Thin cast films of pure polymer were exposed to ethylene oxide as described above. Infrared spectra of both exposed and unexposed polymer were obtained with the Beckman IR-5 spectrophotometer. Figure 8 shows typical spectra of polydimethyl siloxane.

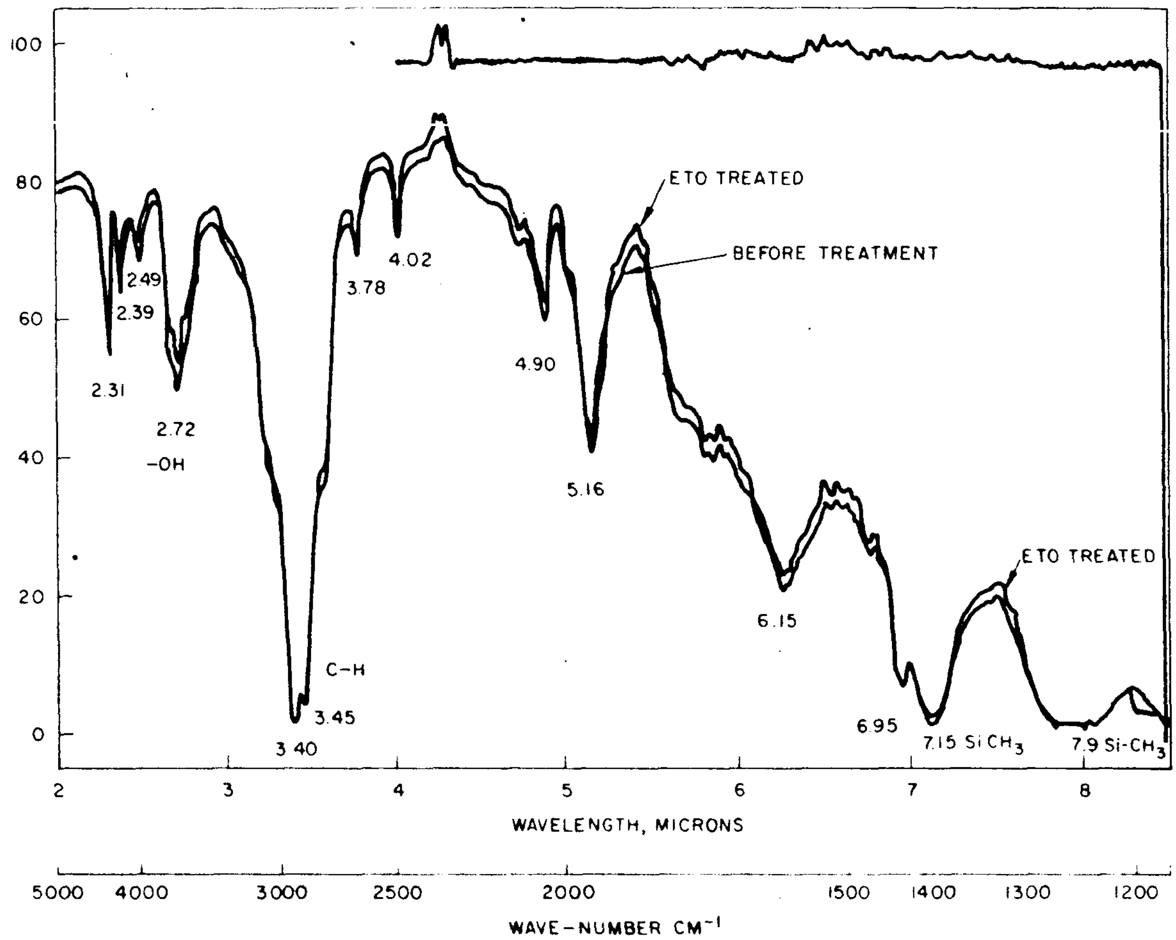



Figure 8. Infrared spectra of polydimethylsiloxane films before and after exposure to ethylene oxide.

TEST DATA

Tables III, IV and V present changes in physical and mechanical properties of materials caused by exposure to dry heat cycling followed by exposure to sterilant gas. Tables VI, VII, VIII and IX present similar data for materials processed through the gas-followed-by-dry-heat-regime. Table X presents sorption data for pure silicone and epoxy compounds.

Physical and mechanical property data for materials screened with the heat-followed-by-gas-regime reflect total change from measurements made after dry heat cycling.

Data for materials tested with the gas-followed-by-heat-regime show change from measurements made on the 'as received' materials.

| Material | Percent Change After Room Temperature ETO-Freon | | Percent Change After 104°F ETO-Freon | |
|---|---|---|---|---|
| | Weight | Volume | Weight | Volume |
| AMS 3303/60 (Silicone) | +0.09 | +0.08 | +0.10 | +0.20 |
| H-Film (Polyimide) | +3.45 | | +3.45 | |
| LS-53/70 (Fluorosilicone) | +0.16 | -0.18 | +0.07 | -0.25 |
| RTV 11 (Silicone) | +0.02 | +0.16 | +0.04 | +0.07 |
| RTV 60 (Silicone) | +0.13 | +0.25 | +0.02 | +0.05 |
| RTV 615 (Silicone) | +0.10 | +0.08 | -0.03 | +0.002 |
| RTV 831 (Silicone) | +0.08 | +0.11 | +0.01 | +0.06 |
| RTV 881 (Silicone) | +0.024 | -0.06 | +0.02 | -0.32 |
| Silgard 182 (Silicone) | +0.02 | +0.01 | +0.01 | +0.0 |
| Tedlar 200 (Polyvinyl fluoride) | +1.0 | | +0.87 | |
| 2-218-S417-7 (Silicone) | +0.07 | +0.13 | +0.08 | 0.0 |
| 4000-80 (Silicone) | +0.14 | +0.11 | +0.17 | +0.06 |
| 7000-80 (Silicone) | +0.06 | +0.10 | +0.06 | +0.10 |

Table III. Weight and volume changes of materials exposed to dry heat cycling and then to sterilant gas.

| Material | After Heat Cycle | After Room Temperature ETO-Frèon 12 | Hardness Change |
|---|---|---|---|
| AMS 3303/60 (Silicone) | 53 | 55 | +2.0 |
| RTV 11 (Silicone) | 54 | 55 | +1.0 |
| RTV 60 (Silicone) | 66 | 67 | +1.0 |
| RTV 615 (Silicone) | 53 | 57 | +4.0 |
| RTV 881 (Silicone) | 45 | 44 | -1.0 |
| Silgard 182 (Silicone) | 57 | 57 | 0.0 |
| 4000-80 (Silicone) | 75 | 77 | +2.0 |
| 7000-80 (Silicone) | 79 | 80.5 | +1.5 |

Table IV. Change in Shore A hardness of materials exposed to dry heat cycling followed by exposure to ethylene oxide-Freon 12 at room temperature (74$^{o}$F).

| Material | After Dry Heat Cycle | | After Room Temperature ETO-Freon 12 | | Percent Change | |
|---|---|---|---|---|---|---|
| | Tensile Psi | Percent Ultimate Elongation | Tensile Psi | Percent Ultimate Elongation | Tensile Psi | Percent Ultimate Elongation |
| AMS 3303/60 (Silicone) | 1065 | 641 | 1090 | 563 | +2.4 | -12.1 |
| 4000-80 (Silicone) | 920 | 300 | 880 | 300 | -4.3 | 0.0 |
| 7000-80 (Silicone) | 938 | 190 | 900 | 200 | -4.0 | +5.2 |

Table V. Change in tensile strength and ultimate elongation of materials exposed to dry heat cycling followed by exposure to ethylene oxide-Freon 12 at room temperature (74$^{o}$F).

| Material | Percent Change After Room Temperature ETO-Freon | | Percent Change After 104°F ETO-Freon | | Percent Change After Dry Heat Cycling | |
|---|---|---|---|---|---|---|
| | Weight | Volume | Weight | Volume | Weight | Volume |
| AMS 3303/60 (Silicone) | +0.07 | +0.2 | +0.05 | +0.07 | -0.007 | +0.05 |
| Epon 828/Z (Epoxy) | +0.1 | | 0.0 | | -0.26 | |
| H-Film (Polyimide) | +1.2 | | | | | |
| Mil-P-13949 (Epoxy Laminate) | +0.02 | | -0.05 | | -0.34 | |
| LS-53/70 (Fluorosilicone) | 0.0 | +0.75 | | | | |
| H-2497 (Micarta) | +0.03 | | -0.01 | | -0.17 | |
| Stycast 1095/11 (Epoxy) | +0.13 | | +0.08 | | -0.7 | |
| Stycast 2651/11 (Epoxy) | +0.04 | | +0.004 | | -0.16 | |
| Tedlar 200 Type 30 B | +0.01 | | | | | |
| 2-218-S417-7 (Silicone) | 0.0 | +0.70 | | | | |
| 4000-80 (Silicone) | +0.21 | +0.14 | +0.23 | 0.12 | -0.007 | +0.20 |
| 7000-80 (Silicone) | 0.06 | +0.05 | +0.03 | 0.08 | +0.006 | +0.27 |

Table VI. Weight and volume changes of materials exposed to sterilant gas and then to dry heat cycling.

| Material | As Received Shore A | After Room Temperature ETO-Freon 12 | Change Shore A | After 104°F ETO-Freon 12 | Change Shore A | After Heat Cycling | Change Shore A |
|---|---|---|---|---|---|---|---|
| AMS 3303/60 (Silicone) | 45 | 44.5 | -0.5 | 48 | +3.0 | 51 | +6.0 |
| 4000-80 (Silicone) | 68 | 66.0 | -2.0 | 73 | +5.0 | 75 | +7.0 |
| 7000-80 (Silicone) | 73 | 71.6 | -1.4 | 78 | +5.0 | 78 | +5.0 |

Table VII. Change in Shore A hardness of materials exposed to sterilant gas and then to dry heat cycling.

| Material | Shore D As Received | After Room Temperature and 104°F ETO Heat Cycle | Change Shore D |
|---|---|---|---|
| Epon 828/Z (Epoxy) | 86.0 | 85.0 | -1.0 |
| H-2497 (Micarta) | 84.5 | 84.0 | -0.5 |
| Mil P-13949 (Epoxy laminate) | 83.0 | 85.0 | +2.0 |
| Stycast 1095 (Epoxy) | 78.0 | 75.5 | -2.5 |
| Stycast 2651 (Epoxy) | 86.5 | 85.0 | -1.5 |

Table VIII. Change in Shore D hardness of materials exposed to sterilant gas and then to dry heat cycling.

| Material | As Received | | After Room Temperature ETO + 104$^{\circ}$F + Heat Cycle | | Percent Change | |
|---|---|---|---|---|---|---|
| | Tensile Psi | Percent Ultimate Elongation | Tensile Psi | Percent Ultimate Elongation | Tensile Psi | Percent Ultimate Elongation |
| AMS 3303/60 (Silicone) | 1030 | 658 | 1000 | 570 | -3.0 | -13.4 |
| 4000-80 (Silicone) | 913 | 300 | 922 | 283 | +1.0 | -5.7 |
| 7000-80 (Silicone) | 932 | 208 | 795 | 200 | -14.7 | -3.9 |

Table IX. Change in tensile strength and ultimate elongation of materials exposed to sterilant gas and then to dry heat cycling.

| Material | Composition | ETO Taken Up Weight Percent | ETO Retained After Vacuum Exposure Weight Percent |
|---|---|---|---|
| Silicone formulation 1 (polydimethyl phenylmethyl siloxane base) | C 1962-34 100 parts<br>triethoxymethyl silane 8 parts<br>dibutyltin dilaurate 2 parts | 3.70 | 0.40 |
| Silicone formulation 2 (polydimethyl siloxane base) | C 1090-61A 100 parts<br>triethoxymethyl silane 8 parts<br>dibutyltin dilaurate 3 parts | 8.30 | 0.00 |
| Silicone formulation 3 (polydimethyl siloxane base) | C 1090-60A 100 parts<br>triethoxymethyl silane 8 parts<br>dibutyltin dilaurate 2 parts | 3.00 | 0.04 |
| Silicone formulation 4 (polydimethyl siloxane base) | C 1090-60A 100 parts<br>triethoxymethyl silane 8 parts<br>dibutyltin dilaurate 2 parts<br>powdered silica 50 parts | 2.61 | 0.06 |
| Epoxy formulation 1 | EPON 828 100 parts<br>methyl nadic anhydride 75 parts | 1.07 | 0.72 |

Table X. Ethylene oxide sorption by silicone and epoxy formulations.

## III. DISCUSSION

Data in Tables III and VI indicate that none of the commercial materials tested displayed an appreciable net change in weight and volume after exposure to sterilant gas followed by vacuum. Table X shows that pure polymers are capable of adsorbing various quantities of ethylene oxide, but retain relatively small amounts after vacuum desorption. Based on these results it would appear that the chief interaction between sterilant gas and materials is physical rather than chemical in nature. This is also borne out by the fact that the amount of sterilant remaining in a material after gas and vacuum exposure decreased when the material was processed through a subsequent heat step. For example, silicone compound 7000-80 retained 0.06 weight percent sterilant gas after room temperature exposure, 0.03 percent after elevated temperature gas exposure, and 0.006 percent after dry heat cycling.

Infrared analysis of a pure silicone compound, polydimethyl siloxane, showed that exposure to ethylene oxide produced no structural change indicating a physical rather than chemical mechanism.

The effect of heat cycling a material prior to gas exposure rather than after can be seen in the change in Shore A hardness experienced with silicone compounds. In general, materials which had not been heat cycled displayed a decrease in hardness when exposed to gas. A slight hardness increase occurs, however, when the same materials is first heat cycled and then exposed to gas.

The decrease in hardness caused by room temperature gas exposure is a reversible effect; an increase is noted after gas exposure at 104°F, and a further increase after dry heat cycling. The dry heat cycle serves to drive off gas adsorbed by base material and by impurities in the material such as curing agents, catalysts, processing solvent and polymer fractions, and also acts as an extended "cure" for elastomers.

Some chemical interaction is indicated by changes in tensile strength of silicone compounds and hardness measurements on epoxy materials (Tables V, VIII and IX). Exposure of silicone compounds AMS 3303/60, and 7000-80 to gas first, and then to dry heat cycling produced a greater decrease in tensile strength than exposure to heat followed by gas. Epoxy compounds Epon 828/Z, Stycast 1095/11 and Stycast 2651/11 showed minor decreases in Shore D hardness when subjected to gas followed by heat. In both cases, the terminal heat cycle may have enhanced rather then retarded gas-material interaction, indicating chemical reaction. In the case of the silicones, the initial heat cycle may have driven off more reactive species before exposure to sterilant gas. Sorption studies with the pure epoxy formulation (Table X) show that materials retained a relatively large amount of ethylene oxide after exposure to vacuum. The manner in which the gas is held in the material can only be established by infrared studies which will be conducted in the next period.

Two problem areas encountered in the commercial products screening portion of the program were electrical property testing and the preparation of test specimens of adhesive materials.

Electrical Tests - Many materials to be tested in this program will find application in electronic assemblies or in electrical systems, therefore the magnitude of electrical property changes caused by gas exposure must be known. Efforts to measure the volume and surface resistivity of elastomeric materials per ASTM D257 were only partially successful. In this method the test specimen is sandwiched between two metal discs, a potential of 500 volts impressed across the electrodes, and the current flow through the test material measured with a highly sensitive ammeter. Because of the high material resistance, currents of less than 1 micro-micro ampere must be measured with comparatively high accuracy. It was not possible to achieve consistent test results for several reasons:

a. Current readings changed with time

b. Any movement of personnel within 10 feet of the apparatus produced drastic fluctuation of the ammeter needle.

The same difficulties were encountered in measuring surface resistivity. Here a potential is impressed across the 1/8" annular space between a metal disc and ring placed on the surface of the test specimen.

We are currently modifying our test apparatus in an attempt to overcome these difficulties, however to be of practical value, data from this program must be coordinated with data from similar materials studies conducted by JPL. Because of the critical nature of electrical testing, test methods and conditions used by Hughes and JPL should coincide. Close coordination with JPL personnel who have cognizance in areas of electrical properties measurement will be required to achieve consistent and useable test information.

Materials - Alternate test specimens of the air-hardening adhesives previously mentioned are currently being prepared in an attempt to obtain test coupons of uniform thickness and texture. For physical property measurements small individual coupons will be fabricated from the silicone materials. It is doubtful that uniform sheets of sufficient size can be produced for mechanical testing, therefore the materials will be used to bond aluminum and silicone elastomer coupons. These in turn will be subjected to tensile testing. The high permeability of elastomers should insure penetration of sterilant gas through the adhesive layer.

Suitable configurations for electrical tests will be determined after further study of the electrical test problem and coordination with cognizant JPL personnel.

## IV. FUTURE WORK

Screening of commercial products will continue with the second JPL list of materials. In the mechanism portion of the program, the following pure polymer systems will be investigated:

1. Epoxy (Shell Epon 828)
    a. Acid cure
    b. Amine cure
2. Polyurethane
    a. Tolylene diisocyanate-Trimethylol propane
    b. Tolylene diisocyanate-Polyethylene glycol
3. Fluorocarbons
    a. Teflon-TFE
    b. Teflon-FEP
4. Polycarbonate
5. Phenolics
    a. Base catalyzed
    b. Acid catalyzed-Novalacs
6. Polyesters

In addition, combinations of polymers and the following metals are to be studied:

1. Copper
2. Silver
3. Gold
4. Nickel
5. Tin
6. Tin-Lead Solder

If time and funding permit, a study will be made of the following:

1. Desorption and sublimation of adsorbed sterilant gas under high vacuum and low temperature conditions. The objective here is to determine the behavior of small quantities of residual sterilant, which are not removed after sterilization procedures, under space-flight conditions.

2. Permeability and diffusion. The permeability of materials to sterilant gas will be studied, and diffusion rates determined.
3. Effects of other sterilization regimes. The effects of subjecting materials to orders of exposure differing from those studied in the present program will be investigated. Materials will be screened by exposing them to dry heat followed by sterilant gas and dry heat, also to sterilant gas followed by dry heat and sterilant gas.

JPL will establish the order of importance of the above tasks and will decide the relative amount of effort to be expended on each. These studies are expected to be exploratory in nature and will be conducted toward the end of the program.

APPENDIX

## APPENDIX

## PURE POLYMER SYNTHESIS AND FORMULATION

The basic synthesis of the polydimethylsiloxane polymer can be represented by the reaction

$$(CH_3)_2SiCl_2 \xrightarrow{H_2O} HO\left(\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array}\right)_x H \ + \ \text{cyclic siloxanes}$$

The resulting polymer is a colorless viscous liquid which can easily be cured into an elastomeric material. Polydimethylsiloxanes can also be prepared by equilibration of cyclic dimethylsiloxanes with either acid or basic catalyst. When an acid catalyst such as sulfuric acid is used, the product has a lower viscosity than when a basic catalyst is employed. A typical equilibration reaction involves the reaction of octamethylcyclotetrasiloxane with concentrated sulfuric acid. This reaction can be written as follows:

$$\left[(CH_3)_2SiO\right]_4 \xrightarrow{H_2SO_4} \left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array}\right]_n$$

<u>Polydimethylsiloxane C1090-60-A.</u> - A six liter three-necked flask fitted with a stirrer, dropping funnel, and thermometer was filled with 3000 ml of water. One liter of dimethyldichlorosilane was added dropwise while stirring vigorously. The temperature was kept in the range of $15^{o}$-$25^{o}C$ by cooling with an external ice-bath. After the addition the mixture was allowed to stand overnight. The upper layer was removed, washed and centrifuged to separate any occluded water. The product was subjected to a distillation at atmospheric pressure. When the pot temperature reached $200^{o}C$ vacuum was applied. The distillation was discontinued when the pot temperature reached $225^{o}C$ under

less than 1 mm pressure. The distillate which consisted mostly of cyclic siloxanes weighed 316 grams. The residue, a colorless heavy oil, weighed 225 grams and was the desired product.

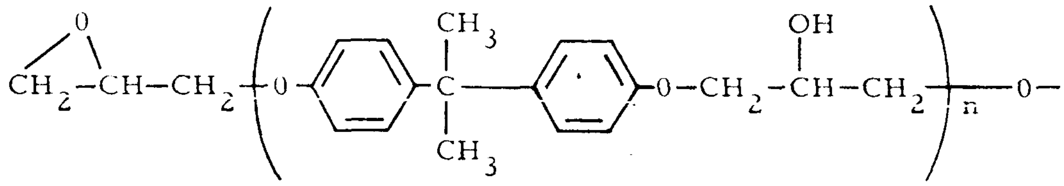
Polydimethylsiloxane C1090-61A. - Into a 500 ml Erlenmyer flask fitted with a magnetic stirrer were added 140 ml of octamethylcyclotetrasiloxane (b.p. 173°-176°C 760 mm Hg), 24.9 ml of concentrated sulfuric acid and 70 ml of diethyl ether. The mixture was stirred for one day during which time considerable increase in viscosity was noted. The reaction product was washed with water a number of times to remove the acid. The ether solution was dried over anhydrous potassium carbonate and subjected to a distillation under vacuum. The distillation was discontinued when the pot temperature reached 210°C and a pressure of 1 mm Hg.

Polydimethyl phenylmethylsiloxane C1962-34. - A mixture consisting of dimethyldichlorosilane (435 ml) and phenylmethyldichlorosilane (180 ml) was added dropwise to 3000 ml of water while stirring vigorously. The temperature during the addition was kept below 35°C using an ice-bath. After the addition the mixture was stirred overnight. The siloxane was separated, washed with water until the washings were free of acid and then subjected to a vacuum distillation to remove the more volatile siloxane fractions. The volatile constituents were chiefly cyclic siloxanes and weighed 122 g. When the pot temperature reached 225°C the distillation was discontinued. The residue weighed 236 g. Based on stoichiometry the structure of the polymer can be approximated by the following formula

$$HO-\left(\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ C_6H_5 \end{array}\right)_x \left(\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array}\right)_{2.44x} -H$$

Epoxy Resins

Many of the epoxy resins are based upon condensation polymers of epichlorohydrin and bisphenol A. These resins are characterized by the formula:



where the value of n determines the viscosity of the resin and other physical properties. There are over a hundred compounds available commercially that can cure these resins because of the presence of both epoxy groups and hydroxy groups as curing sites. For this study the Epon resin types which are marketed by Shell Chemical Corp. and have the above general formula were used. Epon 828 was chosen as the representative resin. It has an average molecular weight of 350, epoxy value of 0.5 and a hydroxyl value of 0.1. Methylnadic anhydride was chosen as a characteristic acid anhydride curing agent. It is a liquid at room temperature and can be readily mixed with the resin to form a more uniform material.

## Pure Polymer Formulations

Silicone Formulation 1

| | |
|---|---|
| Polydimethyl phenylmethylsiloxane (C-1962-34) | 100 parts |
| triethoxymethylsilane | 8 parts |
| dibutyltin dilaurate | 2 parts |

The mixture was maintained at 50$^{\circ}$C for 24 hours, then heated slowly under vacuum up to 150$^{\circ}$C. It was kept at 150$^{\circ}$C for 24 hours under vacuum to remove volatile constituents.

Silicone Formulation 2

| | |
|---|---|
| polydimethylsiloxane (C1090-61A) | 100 parts |
| triethoxymethylsilane | 8 parts |
| dibutyltin dilaurate | 3 parts |

The mixture was kept at 50$^{\circ}$C for 24 hours, then heated slowly under vacuum to 150$^{\circ}$C and maintained at temperature for 24 hours under vacuum to remove volatile constituents.

Silicone Formulation 3

| | |
|---|---|
| polydimethylsiloxane (C1090-60A) | 100 parts |
| triethoxymethylsilane | 8 parts |
| dibutyltin dilaurate | 2 parts |

The mixture was kept at 50°C, heated up slowly to 150°C and kept at that temperature for 48 hours under vacuum.

Silicone Formulation 4

| | |
|---|---|
| polydimethylsiloxane (C1090-60A) | 100 parts |
| triethoxymethylsilane | 8 parts |
| dibutyltin dilaurate | 2 parts |
| powdered silica, 270 mesh | 50 parts |

The mixture was cured for several days at room temperature and then heated up to 150°C and kept at this temperature for 72 hours under vacuum.

Epoxy Formulation 1

| | |
|---|---|
| Epon 828 resin | 100 parts |
| methylnadic anhydride | 75 parts |

The resin mixture was cured by heating to 150°C for 48 hours in air and then under vacuum at 100°C for 24 hours.